Measurement of vapor pressures of some PBDEs and HBCD diastereoisomers

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Introduction

Recently, polybromodiphenyl ethers (PBDEs) with 4 to 7 bromines were newly listed as persistent organic pollutants (POPs) in the Stockholm Convention. Hexabromocyclodocecane (HBCD) is currently under review as the next POPs. To gain a better understanding of the environmental fate and behavior of these brominated flame retardants (BFRs) and human exposure to them, the physicochemical properties of BFRs such as vapor pressure (p_i), water solubility (S_w), and 1-octanol/water partition coefficient (K_{ow}) are of fundamental importance. In our previous works (Kuramochi et al., 2007a and 2007b), we measured the properties except for p_i. From the measurement results, three new findings were obtained: (i) the S_w values of two PBDEs with 4 or 5 bromines (BDE-47 and BDE-99) were similar to those of three HBCD diastereoisomers (α-, β-, and γ- isomers). (ii) K_{ow} of the PBDEs was higher than that of the HBCD isomers. (iii) S_w of HBCD isomers was not the same among the three isomers; it was higher in order of: α- > β- > γ- isomers. Unfortunately, there is little experimental data on p_i. Especially for HBCD isomers, experimental values vary among the literature, and also differ significantly from the values predicted by some methods. In addition, it is experimentally unclear whether there is any difference in p_i among the HBCD isomers. In this study, therefore, p_i of the two PBDEs and HBCD isomers were measured using the gas saturation method, and the temperature dependence of p_i, namely enthalpy of evaporation, was determined. Furthermore, H_w of the PBDEs and HBCDs at 25 ºC was estimated from our previous S_w data of them. Finally, using The OECD P_{ov} & LRTP Screening Tool (Wegmann et al., 2009), we briefly evaluated the P_{ov} (overall persistence) and LRTP (log-range transport potential) of these chemicals.

Materials and Methods

Chemicals: The following PBDEs were used in this study: 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) and 2,2',4,4',5-pentabromodiphenyl ether (BDE-99) purchased from AccuStandard Inc. The purities of BDE-47 and BDE-99 were 100% and 98%, respectively. The used HBCD isomers were α-, β-, and γ-diastereoisomers purchased from Cambridge Isotope Laboratories Inc., with purities ranging from 97.3% to 100%. All of the BFRs were used without further purification.

Vapor pressure (p_i) measurement: Although there are several methods for measuring a very low vapor pressure of upto 10^{-5} Pa, the gas saturation method was used in this work, as shown in Figure 1, because it is scarcely affected by impurity compounds. The apparatus is based on the OECD Guideline for Testing of Chemicals (OECD, 1995) and previous work (Rordorf et al., 1986). In this method, first, a generator column to generate a saturated vapor was made as follows; a 2.2×600-mm stainless steel column was packed with 60–80 mesh glass beads coated with solid sample compound. The weight ratio of solid to glass beads was about 0.2 %. Pure nitrogen gas was flowed as a carrier gas into the

generator column in a thermostated gas oven at a constant flow rate of 20 or 40 mL/min. The sample compound in the saturated vapor was trapped in a mini stainless steel column and a Sep-Pak PS-Air cartridge (Waters). After acetonitrile extraction of the trapped sample from both of them, the concentration of the extraction solution was analyzed by a Waters HPLC -UV system or LC/MC system with a ZQ4000 mass spectrometer. Finally, the p_i value was determined by:

$$p_i = \frac{Q}{V}\frac{RT}{M_w} \qquad (1)$$

where, Q is nitrogen gas volume flowed through the generator column. M_w is molecular weight of sample and R is the ideal gas constant. The experimental temperature ranged from 35 to 100 ºC.

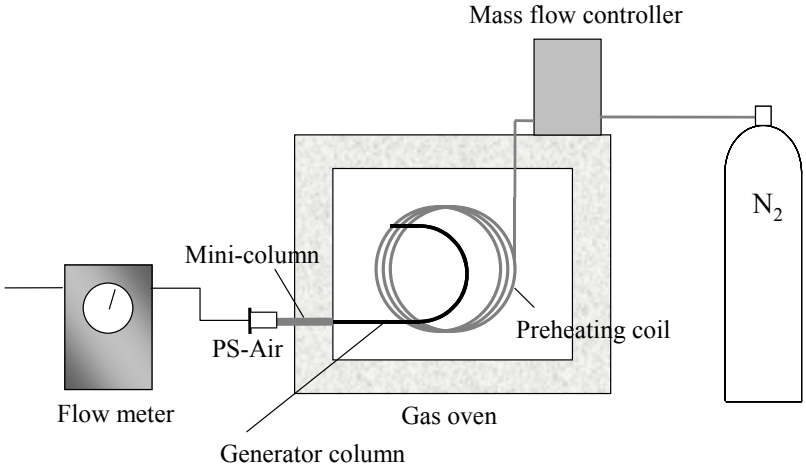

Fig.1. Schematic apparatus of our gas saturation method.

Results and Discussion

To verify the consistency of the gas saturation method, p_i of anthracene (99%, Aldrich) between 35 and 70 ºC was measured, and then compared with literature data (Mackay et al., 2005). The measured p_i values ranged from 0.00279 to 0.164 Pa. These values were in good agreement with the literature data. In terms of reproducibility, the coefficient of variation for the experimental data was within 3 to 6%. These results demonstrate that our apparatus can provide reliable experimental values for very low vapor pressures.

Figure 2 shows the experimental results for PBDEs. p_i of BDE-47 and BDE-99 ranged from 3.18×10^{-4} to 2.56×10^{-2} Pa between 40 and 80 ºC, and from 9.32×10^{-5} to 7.62×10^{-3} Pa between 50 and 90 ºC. As the bromine number of the molecular structure increased, p_i decreased by a factor of 10. From the experimental data, we calculated

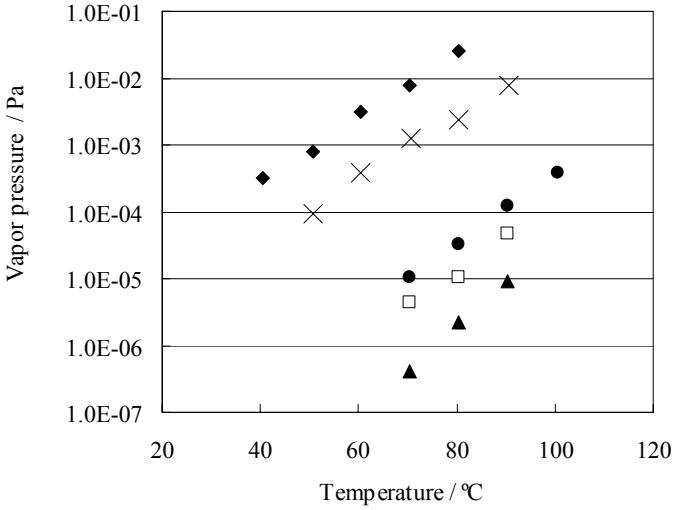

Fig.2. Vapor pressures of two PBDEs and HBCD isomers
♦: Tetra-BDE (BDE-47), ×: Penta-BDE (BDE-99),
●: α-HBCD, □: β-HBCD, ▲: γ-HBCD

the enthalpy of sublimation (ΔH_{sub}), namely temperature dependence of p_i, using the Clausius-Clapeyron equation:

$$\ln p_i = -\frac{\Delta H_{sub}}{RT} + \frac{\Delta S_{sub}}{R} \quad (2)$$

where, ΔS_{sub} denotes the entropy of sublimation. The ΔH_{sub} values of BDE-47 and BDE-99 were 102 and 104 kJ/mol, respectively. The negligible difference between the two compounds indicates that the temperature dependence is independent of the bromine number. In addition, p_i and p^{sl}_i (subcooled liquid vapor pressure) values at 25 ºC were estimated by the Clausius-Clapeyron equation and fugacity ratio derived from the enthalpy of fusion (ΔH_{fus}) and melting point (T_m). The calculated values are listed in Table 1. With respect to p^{sl}_i , the calculated value was compared with the literature data obtained by an indirect method (Wania and Dugani, 2003). The present values were in relatively good agreement with the literature data. This agreement also shows that our measurement method is reasonable for very low vapor pressures of upto 10^{-4} or 10^{-5} Pa.

Table 1. p_i, p^{sl}_i, ΔH_{sub}, and H_w of two PBDEs and three HBCD isomers

	p_i at 25 ºC / Pa	p^{sl}_i at 25 ºC / Pa	p^{sl}_i at 25 ºC / Pa (lit.*)	ΔH_{sub} / kJ•mol^{-1}	H_w / Pa•m^3•mol^{-1}
BDE-47	3.56×10^{-5}	1.12×10^{-4}	2.15×10^{-4}	102	1.18
BDE-99	3.72×10^{-6}	2.20×10^{-5}	3.63×10^{-5}	104	0.480
α-HBCD	1.05×10^{-8}	4.48×10^{-7}	-	128	4.93×10^{-4}
β-HBCD	5.82×10^{-9}	2.48×10^{-7}	-	122	1.33×10^{-3}
γ-HBCD	8.39×10^{-11}	1.00×10^{-8}	-	160	3.59×10^{-5}

*: Wania&Dugani, 2003.

The results for HBCD isomers are shown in Figure 2. The p_i values of three isomers at 80 ºC ranged from 10^{-5} to 10^{-6} Pa, and were much lower than those of BDE-47 and BDE-99 by three or four orders of magnitude. In addition, Figure 3 also shows that the p_i values were different among the three isomers. p_i of α-HBCD was the highest, while p_i of γ-HBCD was lower than those of α- and β-HBCD by one order of magnitude. The ΔH_{sub} values of three isomers were determined by Eq. (2). The ΔH_{sub} value of γ-HBCD was about 1.3 times higher than that of α- and β-HBCD, as given in Table 1. This difference is similar to the difference in enthalpy of fusion. It also indicates that molecular interaction of γ-HBCD is stronger than those of α- and β-HBCD. All the ΔH_{sub} values for HBCDs of p_i, were higher than the two PBDEs.

Based on our previous water solubility (S_w) data of the PBDEs and HBCDs (Kuramochi et al., 2007a and 2007b) and the present p_i values for them, Henry constant (H_w) values of them were estimated by:

$$H_w = \frac{p_i}{S_w} \quad (3)$$

The H_w values are given in Table 1. Although the S_w and K_{ow} of the HBCD isomers were relative close to those of the PBDEs, the H_w values of HBCDs were much lower than those of the PBDEs by three to five orders of magnitude. This indicates that the HBCDs have a much lower partitioning potential to air than both PBDEs due to the lower p_i values of HBCDs. Since important physicochemical properties were available, we tried to calculate the P_{ov} and LRTP (characteristic travel distance (CTD, km) and transfer efficiency (TE, %)) values using The OECD P_{ov} & LRTP Screening Tool. Figures 3a and 3b show the calculation results for not only the PBDEs and HBCDs but also generic PCB homologs (classical POPs-like compounds). The HBCD isomers have lower P_{ov} values compared with the POPs including the PBDEs. However, the LRTP values were close to those of the POPs. The characteristics of the HBCD isomers in terms of P_{ov} and LRTP were similar to those of BDE-47.

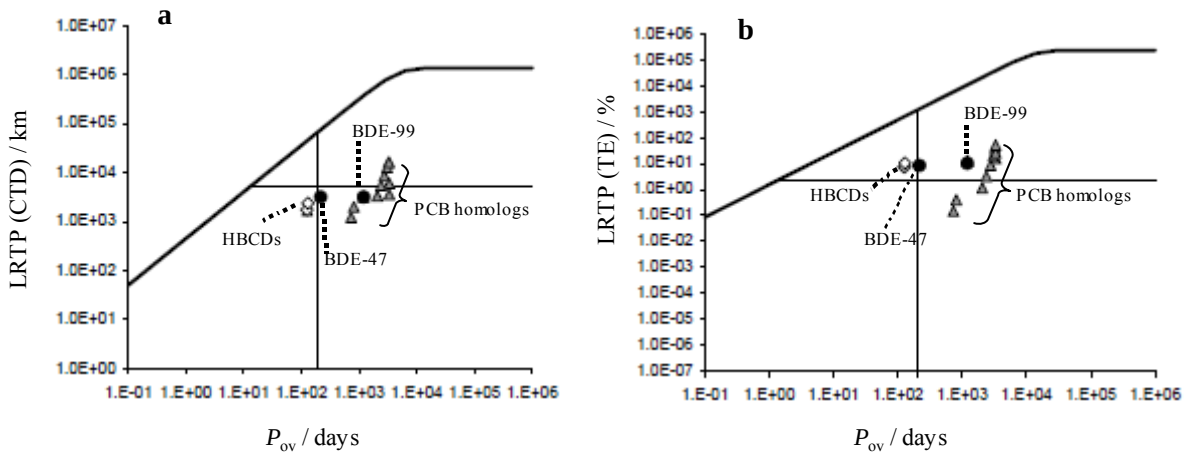

Fig.3. P_{ov} and LRTP (CTD (a) and TE (b)) of two PBDEs (BDE-47 and BDE-99), three HBCD isomers, and PCB homologs calculated by The OECD P_{ov} & LRTP Screening Tool.

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